

Final Technical Report
on
**Experimental Studies on the Physics and
Technology of Polymer Drag-Reduction**

by
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University of Illinois

Urbana, Illinois

July, 2004



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FORWARD

This research was performed in the turbulence laboratory of Thomas J. Hanratty and the polymer laboratory of Anthony J. McHugh. It involved a coordinated effort to relate changes in the turbulent drag reduction properties of several polymer solutions to their rheological and rheo-optical properties. The summary of accomplishments that follows reflects this collaboration. Details on the contributions of the two laboratories are described in the publications listed at the end of the report. This work was carried out over the period 3/19/2001 to 12/18/2003.

Experimental Studies on the
Physics and Technology of Polymer
Drag-Reduction

By

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1. Task Objectives

The introduction of high molecular weight polymer into a flowing liquid can greatly affect the turbulence, leading to a significant decrease in the drag the fluid exerts on solid surfaces. This phenomenon has been of great interest because of its applicability in a number of practical situations.

The focus of this project was the determination of conditions needed to realize large drag-reduction with small concentration of polymers. It had two aspects:

(1) Experimental studies of drag-reduction were carried out in the laboratory of Thomas J. Hanratty in a specially designed flow-loop.

(2) Companion studies were carried out in the polymer laboratory of Anthony J. McHugh so that the performance of drag-reducing polymer solutions can be related to their rheological and rheo-optical properties in simple non-turbulent flows.

The approach that was taken was influenced by the notion that aggregation of polymer molecules could play an important role in determining the effectiveness of the additive. Thus, the focus was on determining the effect of the preparation of the concentrated polymer solutions and their delivery to the flow system and the screening of chemical systems through physical chemical studies.

2. Technical Problems

The demonstration of the importance of aggregates is difficult since their detection in a large flow facility is usually not possible. Therefore, indirect approaches needed to be explored.

The mechanism for forming these aggregates was considered to be of some importance so this matter needed to be given consideration. Specifically, we needed to address the question of how aggregates are formed. Specifically, are they formed in the mixing process or are they formed in the flow field?

Experiments in the flow loop needed to be accompanied by rheological studies of the polymer solutions, which associate their drag-reducing effectiveness with molecular weight and the tendency to form aggregates in a high shear flow.

3. General Methodology

The flow experiments were carried out in a 5x60cm channel, which allowed for optical studies. Concentrated polymer solutions were prepared in a large tank, which was gently mixed with a rotating paddle. Water was circulated in the flow loop with a small pump that had an undersized impeller. The concentrated solution was injected through slots on the wall. Laser-Doppler velocimetry was used to measure the velocity field. In other studies ("ocean experiments"), a batch of polymer solution of the desired concentration was admitted to the flow system. Turbulence was measure with PIV. The solution degraded as it was circulated so changes in the turbulence and the drag could be measured. The degradation process could be expedited by intermittently circulating the solution through a larger pump.

Rheological measurements focused on several aspects. The first involved determination of the shear rate dependence of solution viscosity. Second, molecular weight and molecular weight distributions were determined for the solutions as a function of flow history in both the turbulence channel and in the shear flow rheometry studies using gel permeation chromatography (GPC). Third, rheo-optical analyses of structure formation were carried out using light scattering, birefringence and in situ viscosity measurement under shear flow.

4. Technical Results

(a) *Effects wall roughness*

Studies of the effect of polymer solutions on flow over a well-defined roughened wall were carried out in a test section for which the top wall of the channel was smooth and the bottom wall was a train of sinusoidal waves with a height of 0.5 mm and a length of 5mm. In this way, the behavior over smooth and roughened surfaces could be compared directly in the same experiment. A solution of hydrolyzed polyacrylamide (HPAM) was used. The remarkable feature for both the smooth and rough surfaces was that large effects could be realized with very small concentrations. For example, drag-reductions of 20 percent were observed with concentrations as low as 0.25 ppm and maximum drag-reductions (ca 80 percent) could be realized with 8 ppm.

The turbulence was found to be the same at maximum drag reduction for smooth and roughened walls. Thus, the flow at maximum drag-reduction is independent of the details of the interactions at the wall. Since the drag of water on roughened surfaces is larger than for smooth surfaces, larger drag-reductions could be realized. The turbulence was approximately the same for smooth and rough surfaces if comparisons are made of turbulence velocities that are normalized with the friction velocity. These results are of

interest from a theoretical viewpoint, as well as from a practical viewpoint. They indicate that drag-reduction is not sensitive to the details of the interaction at the wall.

(b) Degradation of drag reduction

The most interesting result emphasizes the importance of joint studies of turbulence and polymer properties. These involved a combined study of the degradation of the drag-reducing properties of the polymer solution and its relationship to molecular weight and the change of molecular weight distribution. Two polymer solutions were used, hydrolyzed polyacrylamide (HPAM) and polyacrylamide (PAM). The first of these is quite stable and the degradation needed to be accelerated by circulating the solution through a larger pump. The second was less stable and required larger concentrations and larger Reynolds numbers to obtain drag reduction. This solution degraded (rather slowly) as it was circulated through the flow loop by the smaller pump.

The remarkable finding was that the molecular weight distribution did not change as the drag-reducing ability of the polymer solution degraded. The usual notion is that degradation in drag reduction is accompanied by changes in molecular weight. We interpret these results by surmising that degradation was accompanied by a breakup of aggregates. Further evidence obtained for this conclusion is the finding (both for PAM and HPAM) that the effectiveness of the drag reduction increases with increases in the concentration of the injected solution. These results, of course, have practical significance in that they emphasize the importance of giving more attention to how the polymer solutions are prepared and delivered.

We should emphasize that we are not suggesting that breakdown in molecular distribution is not important. Thus, in channels with small dimensions, where shear rates can be high, it can be the determining factor. Our message is that both polymer aggregation and molecular weight distribution need to be taken into account in theoretical models of the process.

(c) Heterogeneous drag reduction

The introduction of polymer solutions through tubes located in the flow have been found (in a number of laboratories) to produce threads, which remain intact over large distances, if the injected polymer solution has large concentrations (say, of the order of 6000 ppm). The interesting finding is that (at the same mixed concentration) larger drag reduction can be realized with heterogeneous systems. The mechanism for drag-reduction in these systems is not clearly understood.

Experiments were performed with a slot injection system. A special method was invented to facilitate observations. This involved the mixing of a fluorescent dye with solid polymer particles by gently grinding. A filtering removes the much smaller dye particles that do not adhere to the polymer particles. The resulting dyed polymer particles are gently mixed with water in the same manner as had been done in other experiments.

The use of these dyed polymer solutions revealed that the polymer solutions formed filaments or sheets when injected into the flow, rather than being dispersed molecularly. This could be realized for injected solutions with concentrations as small as 500 ppm. It was found that, for a given mixed concentration in the channel, larger drag reductions were realized when the polymer was in the form of filaments. In fact, at Reynolds number of 6000 and 12000 (based on the half-height of the channel) no drag-reduction was observed if that was not the case.

Because of the importance of understanding mixing in the channel we have developed techniques to study the mechanism of the breakup of filaments. Alumina particles were mixed with the injected polymer solutions. Special lighting techniques and PIV were used to measure the location of the filaments and the velocity inside and outside the filaments. The filaments were found to behave as solid bodies, which break up in high shear regions near a boundary. This seems to explain the observation of a scarcity of filaments close to a wall under heterogeneous drag-reduction conditions that were used. The idea that emerges from this work is that the effectiveness of large filaments does not depend on large scale interactions over the length of the filament. Rather, we feel the breakup creates a heterogeneous distribution of small aggregates, which could be more effective than premixed solutions ("ocean" experiments). We wish that we could have exploited these techniques further – but just ran out of time.

(d) *Rheo-optical results*

A major finding in the rheo-optical studies was that, above a critical shear rate, both the HPAM and the PAM solutions develop turbidity. The range of shear rates where this happens is characteristic of those used in the flow loop.

The flow-induced turbidity shows a dependence on solution shear rate, polymer concentration, and duration of shear that indicates the growth of structures or agglomerates on the size scale of the wavelength of light (632nm) is taking place. Moreover, in a number of cases the turbidity was found to exhibit a pseudo reversible character on cessation of flow, in which the solutions returned to a clear state with a time constant that varied depending on the above-mentioned variables. To our knowledge these are the first in-situ, high quality optical data to show the kinetics of the structuring in drag reducing solutions. Interestingly, on storage in the quiescent state, the sheared solutions eventually develop a pronounced turbidity, on the order of a few days, and eventually precipitate fibrous structures that can be collected and observed microscopically. Apparently the initial structuring, while reversible on short time scales (hours), is still capable of nucleating large scale precipitation on longer time scales (days). At higher concentrations and shear rates the solutions exhibited an irreversible turbidity with larger scale aggregates and precipitated structures forming in the Couette flow cell.

The rheo optical device was also modified to allow measurement of in-situ small angle light scattering patterns under flow. Such patterns are amenable to analysis

allowing quantification of size scales of the flow-induced structures in terms of the small angle scattering structure factor. Results for the size and time scales of formation and relaxation of the flow-induced scattering structures correlated closely with estimates made applying Mie light scattering theory to the turbidity data. Fits of the turbidity and structure factor independently demonstrate the presence of micron-sized structures forming under shear flow.

One of the original notions in carrying out rheo-optical studies was to determine whether structure formation could be induced in the turbulent flow field. The tendency for drag-reducing polymer solutions to form structures in a controlled flow environment encourages such an interpretation. However, the evidence for this is not strong. For example, drag-reducing solutions that are slightly degraded in the flow loop show no evidence of structure formation in the rheo-optical device.

(e) Viscosity measurements

Rheological studies were made with a TA Instruments, AR1000-N rheometer. Measurements were made using a cone-and-plate geometry with a 6 cm, 0.29° cone and a gap of 13 mm. Viscosity measurements provided a simple way to monitor degradation in polymer solutions. The steady state viscosity was found to decrease as solutions lose their effectiveness in reducing drag.

Shear thinning behavior, usually seen in high molecular weight polymer solutions, was seen in the HPAM polymer solutions. No change in viscosity was observed for shearing times less than one minute for shear rates below $\sim 1000 \text{ s}^{-1}$. For longer shear times and higher shear rates, the shear stress (torque) exhibited a time-dependent increase (rheopexy) for undegraded solutions. The rheopexic behavior at 1000 and 2000 s^{-1} give evidence that shear-induced structuring was occurring. These results also correlated well with the rheo-optical experiments showing shear-thickening and turbidity development under the same conditions

Summary of important findings and conclusions

(a) Effect of aggregation

There are numerous papers, which suggest that drag-reduction increases with increased molecular weight of the polymer molecules. Several aspects of our work point to the idea that aggregation of polymers can greatly enhance their ability to alter the turbulence. The most surprising of these is the finding that for hydrolyzed polyacrylamide (HPAM) and for polyacrylamide (PAM) different drag-reductions can be realized for solutions with approximately the same molecular weight distribution. These results were obtained when degrading homogeneous polymer solutions by sending them through a pump. Degradation under these circumstances had to occur through breakup of polymer aggregates.

We conclude that drag reduction effectiveness increases with molecular weight and with aggregation. A corollary is that degradation in drag reduction occurs by the breakup of aggregates and/or the breakup of molecules.

(b) Effect of filaments

We find that, under certain circumstances, concentrated polymer solutions (as low as 500 ppm) delivered through wall slots form large filaments similar to those formed by injecting polymers through a capillary tube into the bulk flow (usually at concentrations greater than 1000 ppm). Larger drag reductions are realized, at the same mixed concentration, when these large filaments are present. We do not understand how the filaments are formed. One possibility is that very small gel particles form into larger particles in the delivery piping. Another is a consequence of injecting a high viscosity polymer solution into lower viscosity water. The drag reduction does not seem to depend on the continued existence of these large filaments. In fact, as the solution circulates through the system, the large polymer filaments break up – however, large drag reduction could still be maintained. We believe that the effectiveness of the filaments could result because their breakup insures the presence of small aggregates (of, perhaps, only a few molecules), which are the real cause of the reduction of the turbulence for these systems. (Of course, this is speculation).

(c) Effect of injection

We have carried out experiments with completely mixed solutions ("ocean" experiments) and with solutions formed by injection of a concentrated solution into the flow channel. In general, better results are obtained with injection and the amount of drag-reduction increases with increases in the concentration of the injected solution.

(d) Chemistry

An important result is the finding that hydrolyzed polyacrylamide is much superior to polyacrylamide, both from the view-point of the amount of drag-reduction and the degradation of the polymer solution. Chemistry is important.

(e) Other results

Most large scale operations will involve conditions where the surface will be hydraulically rough. Since the mechanism for sustaining wall turbulence is different for smooth and rough surfaces, it is of importance to know whether experiments with smooth surfaces are applicable. Our studies with roughened surfaces are encouraging in this respect. Here, we have found larger drag-reductions with hydraulically rough surfaces. However, these studies could also have a message for the modelers.

5. Special comments and implications for further research

We feel that the work on the application of drag-reducing polymers will be enhanced by a better understanding of the effects of chemistry, of polymer mixing and on the method of polymer delivery. We strongly recommend that these types of studies should be a part of future research.

Thus, if polymer filaments are beneficial for drag reduction we should design injection methods and choose chemical systems, which produce them. The implications of having a sea water environment should be an important consideration. Our experiments suggest that, in many cases, drag reduction is enhanced by aggregates, which are not easily detected by standard flow visualization techniques. The development of imaginative ways to observe these aggregates would be of great interest. This could involve supplementing studies in a flow loop with experiments in a smaller scale, specially designed equipment.

The mixing and breakup of filaments in a turbulent flow could be an important ingredient in modeling the behavior of a drag-reducing system. More information on these processes is needed. The special PIV/visual technique explored in this research should be exploited further to study fundamental aspects of the mixing process. The rheo-optical techniques could provide a valuable tool in studying the formation of aggregates in a shear flow and in screening polymer systems with regard to their possible drag reduction effectiveness.

Appendix 1 – Manuscripts giving details on the work.

Publications

(1) M. Vlachogiannis, M.W. Liberatore, A.J. McHugh and T.J. Hanratty. Effectiveness of a drag-reducing polymer: relation to molecular weight distribution and structuring. Physics of Fluids, 15:3786-3794, 2003.

Solutions of partially hydrolyzed polyacrylamide were degraded by intermittent circulation through a large pump in a turbulent flow loop. Degradation was not accompanied by significant changes in the molecular weight distributions. This observation suggests that, for the system studied, clusters or aggregates of polymers have a more important effect on the turbulence than individual molecules. Therefore, degradation occurs by the destruction of these clusters.

(2) M.W. Liberatore, S. Baik, A.J. McHugh and T.J. Hanratty. Turbulent Drag Reduction of Polyacrylamide Solutions: Effect of Degradation on Molecular Weight Distribution. Journal of Non-Newtonian Fluid mechanics, accepted, June, 2004.

The circulation of solutions of PAM in a flow loop is accompanied by decreases in the drag reduction and a very gradual change in the molecular weight distribution. However, there are large time periods over which drag reduction is decreasing and the molecular weight distribution is not changing. This suggests that polymer aggregation could be an important factor in understanding and applying polymer drag reduction.

(3) M. Vlachogiannis, T.J. Hanratty. Influence of Wavy Structured Surfaces and large scale polymer structures on drag reduction. Exp. in Fluids (2004), 36 (5), 685-700.

This paper makes several contributions: (a) It shows that polymer drag reduction for smooth and structured surfaces are similar even though the interaction with the wall can be quite different in these two cases, (b) Injection of concentrated polymers through a wall slot can create large filamentous structures which are convected downstream. Larger drag-reduction can be realized when these structures are present.

(4) S. Baik, M. Vlachogiannis, T.J. Hanratty. Use of PIV to study heterogeneous drag reduct. submitted to Exp. Fluids, 2003.

PIV techniques were developed to examine how large filamentous structures behave in a turbulent field. The filaments behave like solid bodies, which break up in high, shear regions near a boundary. The study of the breakup process suggests that a heterogeneous distribution of small aggregates of polymers could be more effective than uniformly distributed molecules. This paper summarizes work with PAM and HPAM, which shows that solutions formed by injection (even when large filaments are not present) are more effective than “homogeneous” premixed solutions.

(5) M.W. Liberatore and A.J. McHugh. Dynamics of Shear-Induced Structure Formation in High Molecular Weight Aqueous Solutions. Journal of Non-Newtonian Fluid Mechanics, submitted 2003.

Shear-induced structure formation in solutions of drag-reducing polymers has been studied for aqueous solutions of high molecular weight partially hydrolyzed

polyacrylamide, polyacrylamide, and poly (ethylene oxide). Under high shear flow, increasing turbidity is accompanied by growing lozenge- or butterfly-shaped scattering patterns. With increasing shear, dichroism increases and the orientation angle approaches zero, i.e., scattering centers are aligning with the flow. Fits of the turbidity and structure factor independently demonstrate the presence of micron-sized structures forming under shear flow.

(6) M.W. Liberatore, E.J. Pollauf and A.J. McHugh. Shear-induced structure formation in solutions of drag reducing polymers. Journal of Non-Newtonian Fluid mechanics, 113:193-208, 2003.

Aqueous solutions of high molecular weight partially hydrolyzed polyacrylamide, polyacrylamide, and poly(ethylene oxide) were examined in the concentration range of 100 to 4000 ppm by weight. Solutions exhibited rheopexy and turbidity patterns under high shear, indicative of structure formation. The sheared solutions also developed irreversible, large-scale turbidity and eventual precipitation on quiescent storage over several days.

Theses

Pollauf, Emily Jean, Rheology of Drag Reducing Polymers, M.S. Thesis, University of Illinois at Urbana-Champaign, 2002.

Liberatore, Matthew Walter, Dynamics of Flow-Induced Structure Formation in Drag Reducing Polymer Solutions, Ph.D. Thesis, University of Illinois at Urbana-Champaign, 2003.

Appendix 2

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